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The Crystal Structures of a Series of Cubic Hydrogen Insertion Compounds of the Mixed Molybdenum Tungsten Oxides

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The structures of three hydrogen insertion compounds, $D_{0.56}Mo_{0.25}W_{0.75}O_3$, $D_{0.80}Mo_{0.5}W_{0.5}O_3$, and $D_{0.81}Mo_{0.69}W_{0.31}O_3$, were determined from powder neutron diffraction studies. All three compounds were body centered cubic (space group *Im*3) with the unit cell containing eight formula weights. The lattice parameter a = 7.5558(6), 7.587(1), and 7.5743(5) Å, respectively. A least-squares method based on peak intensities was used to determine the structures. The metal atoms lie on the special perovskite sites and are surrounded by nearly regular octahedra of oxygen atoms with the latter displaced from the normal perovskite positions along ⟨110⟩. The deuterium atoms are distributed over 48 sites in the unit cell and form —OD bonds directed toward the nearest oxygen atom in a neighboring octahedron. These compounds have the same structure as the cubic hydrogen tungsten bronze $H_{0.53}WO_3$. © 1986 Academic Press, Inc.

Introduction

The hydrogen insertion compounds formed by MoO_3 and WO_3 are well known (*1–6*). Recently the authors have prepared and characterized a series of hydrogen insertion compounds of the mixed molybdenum tungsten oxides $Mo_yW_{1-y}O_3$ ($0.1 < y < 0.9$). The compounds $H_xMo_yW_{1-y}O_3$ form a tetragonal phase with $0.1 < x < 0.2$ and a cubic phase when $x > 0.35$ (*7*). These phases appeared to have structures closely related to those formed by H_xWO_3 (*1*) rather than H_xMoO_3 (*6*). Powder X-ray studies of the cubic phase revealed weak superlattice lines similar to those found for $D_{0.53}WO_3$ (*8*) indicating the unit cell was body centered rather than simple cubic. In the present work the crystal structures of three of the cubic phase hydrogen insertion compounds were determined.

Sample Preparation and Characterization

$Mo_yW_{1-y}O_3$

The mixed metal oxides were prepared as follows:

$Mo_{0.25}W_{0.75}O_3$. By cocrystallization of ammonium molybdate (AnalaR) and ammonium paratungstate (Fluka) followed by oxidation at 500°C.

$Mo_{0.5}W_{0.5}O_3$. Reaction of MoO_3 and WO_3 in a sealed silica tube at 700°C.

$Mo_{0.69}W_{0.31}O_3$. By oxidation at 500°C of the precipitate produced on adding an aqueous solution of the mixed ammonium metallates to ethanol.

The oxides were analyzed by evaporation of MoO_3 at 800°C and by using X-ray

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microanalysis, which also showed the samples to be homogeneous.

$D_xMo_yW_{1-y}O_3$

Deuterium was inserted into the mixed metal oxides using deuterium gas in the presence of a platinum catalyst (*3*). An aqueous solution of H_2PtCl_6 was added to the metal oxide and the solvent removed by evaporation at 100°C. Deuterium gas was then dosed onto the samples at 298 K to give the required composition. The composition was checked using the method of Choain and Marion (*9*). The final samples contained 1.6% Pt by weight; one sample, $D_{0.81}Mo_{0.69}W_{0.31}O_3$, which had been prepared from a previously reduced oxide sample reoxidized at 500°C, showed reflections due to platinum in the powder X-ray pattern; these were not visible in the powder patterns for the other compounds. The cubic lattice parameter for each of the hydrogen insertion compounds was determined from powder X-ray data.

Neutron Diffraction

Neutron diffraction measurements were carried out at room temperature using the powder diffractometers PANDA ($D_{0.81}Mo_{0.69}W_{0.31}O_3$) and 10HPD ($D_{0.56}Mo_{0.25}W_{0.75}O_3$ and $D_{0.80}Mo_{0.5}W_{0.5}O_3$) at AERE Harwell. The samples were loaded into 12-mm vanadium cans sealed with rubber O rings to prevent sample decomposition of the air-sensitive compounds.

For $D_{0.56}Mo_{0.25}W_{0.75}O_3$ and $D_{0.80}Mo_{0.5}W_{0.5}O_3$, a wavelength of 0.9946 Å was used and 15 Bragg intensities were collected in the 2θ range 10–65°. For $D_{0.81}Mo_{0.69}W_{0.31}O_3$, a wavelength of 1.1495 Å was used and data were collected over the 2θ range 5–90°. For this sample, platinum peaks could be detected and peaks overlapping these were excluded from consideration; 14 Bragg intensities were determined. The powder neutron patterns were consistent with a body centered cubic unit cell.

The atom positions were refined using a computer program written by Wiseman (*10*). This program minimizes the function

$$\sum_i w_i(I_{\mathrm{obs}_i} - I_{\mathrm{calc}_i})^2.$$

The weighting factor w_i was taken as $1/\sigma_i^2$ where σ_i is the standard deviation of the ith intensity as estimated from counting statistics. The neutron scattering lengths used were $b_D = 0.667 \times 10^{-14}$ m, $b_{Mo} = 0.69 \times 10^{-14}$ m, $b_W = 0.48 \times 10^{-14}$ m, and $b_O = 0.58 \times 10^{-14}$ m (*7*).

Structure Refinements

The atom positions found by Wiseman and Dickens for $D_{0.53}WO_3$ (*8*) were used as the initial parameters for the structure refinement. The molybdenum and tungsten atoms were placed on the 8(*c*) ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) position with the fractional occupancies given by the respective formulae. The oxygen atoms were placed on 24(*g*) (0, *y*, *z*) positions, with $y + z$ constrained to equal 0.5, thus effecting the tilting of almost regular octahedra and producing a square of oxygen at-

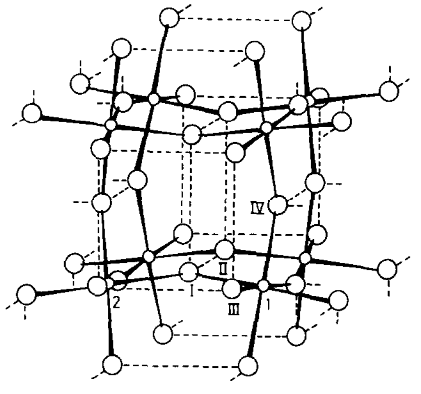

FIG. 1. The eight MO_6 octahedra around (0, 0, $\frac{1}{2}$) in $D_xMo_yW_{1-y}O_3$. Large circles represent oxygen atoms and small circles Mo/W atoms.

oms around the 6(*b*) (0, 0, ½) position as shown in Fig. 1. The 48 deuterium sites in the unit cell are described by 24(*g*), (0, y_1, z_1) and (0, y_2, z_2), the 8 possible sites within the square of oxygens are shown in Fig. 2. The constraints $y_1 + z_2 = 0.5$ and $z_1 + y_2 = 0.5$ were used to maintain the equality of the deuterium atoms and reduce the number of variables; their temperature factors and occupation numbers were constrained to be equal. The temperature factors for molybdenum and tungsten atoms were constrained to be equal, giving an average scattering length for the metal atoms.

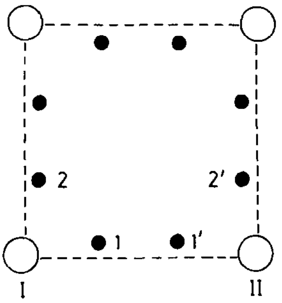

FIG. 2. Statistically occupied deuterium sites (small filled circles) within the square of oxygen atoms (large circles) in $D_xMo_yW_{1-y}O_3$.

TABLE I

OBSERVED AND CALCULATED INTENSITIES

	$D_{0.56}Mo_{0.25}W_{0.75}O_3$			$D_{0.80}Mo_{0.5}W_{0.5}O_3$			$D_{0.81}Mo_{0.69}W_{0.31}O_3$		
k k l	I_{calc}	I_{obs}	$\sigma(I_{obs})$	I_{calc}	I_{obs}	$\sigma(I_{obs})$	I_{calc}	I_{obs}	$\sigma(I_{obs})$
2 0 0	31.7	31.9	0.33	22.5	22.1	0.30	21.4	20.5	0.22
3 1 0	27.3	26.6	0.31	30.6	32.1	0.30	25.7	26.0	0.20
2 2 2	9.72	9.08	0.31				2.56	2.58	0.15
3 2 1	17.6	17.8	0.29	15.3	14.0	0.26	14.1	15.2	0.26
4 0 0	33.3	34.3	0.32	25.1	25.2	0.27	24.3	25.0	0.20
4 2 0	32.5	32.6	0.33	27.9	27.2	0.26	3.65	3.20	0.18
4 2 2				3.08	3.64	0.17			
4 3 1 5 1 0	6.75	6.00	0.24	5.01	4.79	0.22	5.75	3.75	0.20
5 2 1	4.06	4.81	0.22	3.07	3.99	0.20			
4 4 0	16.0	15.1	0.26	9.34	10.1	0.20	9.94	11.5	0.30
4 3 3 5 3 0	16.3	16.4	0.26	15.0	14.6	0.24	15.4	15.4	0.25
4 4 2 6 0 0	12.7	12.5	0.26	10.1	9.27	0.22	9.90	10.8	0.30
5 3 2 6 1 1	16.9	17.1	0.28	12.9	13.1	0.24	13.7	14.4	0.26
4 4 4	4.48	5.02	0.23	2.50	3.33	0.18	2.41	2.64	0.50
5 4 3 5 5 0 7 1 0	14.7	14.8	0.26	11.4	12.3	0.24	12.0	11.1	0.30
5 5 2 6 3 3 7 2 1	10.4	10.3	0.25	8.11	7.41	0.21	8.46	7.52	0.36
	$R_I = 2.46\%$ AF = 2.75			$R_I = 4.96\%$ AF = 4.71			$R_I = 5.84\%$ AF = 5.54		

TABLE II

Refined Atomic Parameters

	$D_{0.56}Mo_{0.25}W_{0.75}O_3$				$D_{0.80}Mo_{0.5}W_{0.5}O_3$				$D_{0.81}Mo_{0.69}W_{0.31}O_3$			
Atom	y	z	$B(\text{Å})^2$	Occ	y	z	$B(\text{Å})^2$	Occ	y	z	$B(\text{Å})^2$	Occ
D(1)	0.071(5)	0.326(5)	2.1(0.8)	0.093	0.067(5)	0.330(5)	1.6(1.1)	0.133	0.062(9)	0.319(6)	2.8(1.7)	0.135
D(2)	0.174(5)	0.429(5)	2.1(0.8)	0.093	0.170(5)	0.433(5)	1.6(1.1)	0.133	0.181(6)	0.438(9)	2.8(1.7)	0.135
O	0.213(1)	0.287(1)	1.2(0.1)	1.0	0.208(1)	0.292(1)	1.5(0.2)	1.0	0.207(1)	0.293(1)	1.4(0.3)	1.0
Mo			1.4(0.3)	0.25			1.7(0.5)	0.5			1.5(0.5)	0.69
W			1.4(0.3)	0.75			1.7(0.5)	0.5			1.5(0.5)	0.31

Space group $Im3$ cubic

$D_{0.56}Mo_{0.25}W_{0.75}O_3$	$a = 7.5558(6)$ Å
$D_{0.80}Mo_{0.5}W_{0.5}O_3$	$a = 7.587(1)$ Å
$D_{0.81}Mo_{0.69}W_{0.31}O_3$	$a = 7.5743(5)$ Å

Unit cell contains 8 × $D_xMo_yW_{1-y}O_3$

Atoms on

D(1)	24(g)	$(0, y, z)$
D(2)	24(g)	$(0, y, z)$
O	24(g)	$(0, y, z)$
W	8(c)	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$
Mo	8(c)	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$

In the final refinements the scale factor, 3 positional parameters and 3 isotropic temperature factors were refined.

The observed and calculated intensities are shown in Table I and the positional and thermal parameters are given along with the estimated standard deviations in Table II. The reliability index R_I is a measure of the validity of the model and is given by

$$R_\text{I} = \sum_i 100|I_{\text{obs}_i} - I_{\text{calc}_i}| \Big/ \sum_i I_{\text{obs}_i}.$$

The agreement factor AF is given by

$$\text{AF} = \left\{\sum_i w_i(I_{\text{obs}_i} - I_{\text{calc}_i})^2/(m - n)\right\}^{1/2}$$

where m is the number of observations and n the number of independent parameters. Relaxation of the constraints applied to the deuterium and oxygen atom positions produced no significant improvement in the agreements.

Discussion

Some important bond distances and angles for the cubic hydrogen insertion compounds, $D_xMo_yW_{1-y}O_3$, are listed in Table III. Data for $D_{0.53}WO_3$ from (*8*) is included for comparsion. All the compounds have the same basic structure. The metal atoms are arranged on a primitive cubic lattice, surrounded by almost regular octahedra of oxygen atoms, linked together by shared vertices. The octahedra are titled from the *M–M* direction producing a shortened *O–O* distance between adjacent octahedra. The titling of octahedra, and the distortions which result, have been classified by Glazer (*11*). All the above compounds are in the $(a^+a^+a^+)$ group with equal tilts about each axis. These tilts convert 8 twelve-coordinate *A* sites of the original perovskite structure to 2 A' sites and 6 A'' sties. Around the A' sites all the oxygen atoms have been displaced outward. Around the A'' sites, the local environment is provided by 4 oxygen atoms displaced inward along the diagonals of a square toward the original *A* site.

The deuterium atoms are statistically attached to oxygen atoms in the square to form deuteroxyl bonds. The O–D distances are all ~1.10 Å. The deviations from a normal O–H bond length of 1 Å may be caused

TABLE III

BOND ANGLES AND DISTANCES

	$D_{0.56}Mo_{0.25}W_{0.75}O_3$	$D_{0.80}Mo_{0.5}W_{0.5}O_3$	$D_{0.81}Mo_{0.69}W_{0.31}O_3$	$D_{0.53}WO_3$[a]
	Bond distances (Å)			
M1–M2	3.7779(3)	3.794(1)	3.7872(3)	3.781
M1–OI	1.930(2)	1.950(2)	1.949(3)	1.926
OI–OII	3.219(11)	3.156(11)	3.136(11)	3.264
OI–OIII	2.700(6)	2.720(6)	2.717(2)	
OIII–OIV	2.758(8)	2.794(8)	2.794(5)	
OI–D1	1.11(4)	1.11(5)	1.12(10)	1.10
D1–OII	2.17(1)	2.11(1)	2.05(1)	
D1–D1′	1.07(5)	1.02(5)	0.94(10)	
D1–D2	1.10(5)	1.11(5)	1.27(8)	
D1–D2′	2.01(5)	1.96(5)	2.05(9)	
	Bond angles (°)			
OI–M1–OIII	88.8(1)	88.4(1)	88.4(1)	
OI–M1–OIV	88.8(1)	88.4(1)	88.4(1)	
OIII–M1–OV	91.2(1)	91.6(1)	91.6(1)	
M1–M2–OI	11.8(3)	13.4(3)	13.7(1)	11.0
M1–OI–M2	156.3(6)	153.2(6)	152.6(6)	158.1
D1–OI–OII	15.4(2.5)	14.7(2.5)	11.4(4.0)	
M1–OI–D1	100.2(2)	101.5(2)	101.2(2)	

[a] From Ref. (*8*).

by relaxation of the oxygen atoms from their average position on attachment to a deuterium atom.

Coherent neutron diffraction affords no information about the local distribution of the deuterium atoms and gives only the average contents of a unit cell. However, certain deuterium atom arrangements within the square can be eliminated, since they would lead to impossibly short interactomic distances. Nuclear magnetic resonance is sensitive to the local proton environment and a sample of $H_{0.80}Mo_{0.5}W_{0.5}O_3$ gave a second moment of 2 G^2 in the rigid lattice region (*12*). Such a small value precludes the existence of OH_2 groups in the structure and agrees well with the value of 2.2 G^2 calculated for a random distribution of hydrogen atoms over the possible sites (excluding simultaneous occupation of sites separated by chemically unreasonable distances).

Comparisons between the individual compounds show that

(1) The metal–oxygen bond length increases, as the mean oxidation state of the metal decreases and does not depend on the Mo/W ratio.

(2) The tilting of the octahedra increases with the deuterium content of the insertion compounds.

(3) The O–O distance decreases, as the deuterium content of the compounds increases with effect 2 dominating 1.

The tilting of the octahedra and shortening of the O–O distance with increasing deuterium content is presumably driven by the formation of a weak hydrogen bond. A number of compounds $MO_{3-x}(OH)_x$ with similar structures are known. For $HNbO_3$ a rectangle rather than a square of oxygen atoms is formed (*13*, *14*) with O–O distances of 2.90 and 3.22 Å, giving a stronger hydrogen bond. In the hydroxides of formula $M(OH)_3$ there are sufficient hydrogens to hydrogen bond to all the oxygens and much shorter O–O distances result. For example for $In(OD)_3$ (*15*), $Lu(OH)_3$ (*16*), and $Sc(OH)_3$ (*17*) the shortest O–O distances are 2.733, 2.728, and 2.87 Å, respectively. Again for the nonstoichiometric $H_{1.36}ReO_3$ (*18*) a rectangle rather than a square of oxygens is found.

Acknowledgments

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